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(54) Title: SPHERICAL MICROPARTICLES HAVING AN INNER WAX COATING DEPOSITED AROUND BIOLOGICALLY ACTIVE COMPOUNDS

## (57) Abstract

The invention relates to essentially spherical microparticles comprising a biologically active compound as core substance and a polymeric capsule material, wherein a hydrophobic wax forms a wax film as interlayer on the inner polymeric capsule wall and wholly or partially encapsulates the active ingredient. The invention further relates to a process for the preparation of the microparticles, to the use thereof for the preparation of a composition for controlling plant pests, weeds or animal parasites, as well as to aqueous spray mixtures, water-dispersible granulates or water-dilutable powders containing the claimed microparticles.

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Spherical microparticles having an inner wax coating deposited around biologically active compounds

The present invention relates to a process for the preparation of spherical microparticles which contain biologically active compounds and which are provided at the inner capsule wall with an additional wax layer deposited around the biologically active compound. The invention also relates to the use of said microparticles for the preparation of a composition for controlling plant pests, weeds or animal parasites as well as to aqueous spray mixtures containing the microparticles obtained in the practice of this invention.

The microencapsulation of active ingredients in polymeric materials with different polymers is known and can be carried out by various methods, as described for example in Encyclopedia of Polymer Science, John Wiley Sons, 1968, Vol. 8, pp. 719-736.

Some typical microencapsulation methods are: coacervation, interfacial polymerisation at liquid-liquid surfaces or interfacial polycondensation, for example at a solid phase boundary. In addition to these chemical methods, other suitable methods are physical methods such as the microencapsulation of aerosols. Amino resins are often used as polymeric encapsulating materials for microparticles that contain agrochemical compounds. An overview of the broad field of use of these resins for microencapsulation is given, inter alia, in Acta Polymerica 40, (1989) No. 4, pp. 243-251.

Particular demands are made of the release properties of biologically active agrochemicals. On the one hand, the applied microparticles must be comparably active in field application to e.g. emulsifiable concentrates. In addition, they shall release the active ingredient uniformly over an extended period of time. On the other hand, virtually no active ingredient shall be released on skin contact, so that a high degree of handling safety is ensured.

The preparation and properties of microparticles prepared with self-crosslinking amino resins are described in Acta Polymerica 40, (1989) No. 5, pp. 325-331. In the processes referred to therein, the starting materials are solid compounds which are e.g. additionally ground to give a fine dispersion in the aqueous polymer solution and are then encapsulated. The drawback of this process is that the solid materials have to be ground to an average particle size of c. 10-30  $\mu\text{m}$ . The addition of active ingredients in the liquid, dissolved or melt state is therefore usually of interest.

EP-A-0 368 576 teaches, inter alia, that the insecticide chlorpyrifos is unstable to hydrolysis and, depending on the pH range, can rapidly lose its biological activity under the influence of water. Especially in termite control, the active ingredient must have good stability to hydrolysis in the alkaline range, as it is frequently applied to concrete. Another solution is to provide formulations in which the contact with water is greatly retarded, while the biological activity still remains intact. Such formulations must have release properties sufficiently effective to ensure reliable control of the termites. In addition to this specific stability in the alkaline range, another usual requirement is that of superior long-term stability under all climatic conditions, especially rain and tropical climate. Microencapsulations having more or less strongly hydrophilic capsule walls - depending on the polymer employed - can have drawbacks as regards their long-term stability.

It has now been found that these drawbacks of inadequate long-term stability and limited stability to hydrolysis of the capsule core can be substantially overcome if the microcapsules contain, in addition to the active ingredient, a hydrophobic wax such that the wax forms a film that surrounds the active ingredient on the inner microcapsule wall. Penetration of water into the capsule core is thereby hindered, while the release properties remain effective enough to achieve sufficiently good activity.

The active ingredient is released approximately uniformly over an extended period of time from the microparticles, so that a good activity is achieved.

In one of its aspects therefore the invention relates to essentially spherical microparticles comprising a biologically active compound as core substance and a polymeric capsule material, wherein a hydrophobic wax forms a wax film as interlayer on the inner polymeric capsule wall and wholly or partially encapsulates the active ingredient.

Depending on the capsule size, the average thickness of the wax layer can be from 1 nm to 1  $\mu\text{m}$ . Preferably it is from 5 nm to 100 nm. The wax layers are not completely uniform, but have slightly different thicknesses.

The spherical microparticles preferably have an average diameter of 0.5 to 500  $\mu\text{m}$ . More preferably the microparticles have an average diameter of 0.5 to 100  $\mu\text{m}$  and, most preferably, of 0.5 to 20  $\mu\text{m}$ .

The polymeric wall material is preferably 5 to 40 % by weight of the total weight of the microparticles.

The polymeric wall material may consist of a polyacrylate, a polyurethane, a polyester or an amino resin.

The polymeric wall material is preferably an amino condensation resin, most preferably a polycondensate of melamine and formaldehyde, a wholly or partially etherified melamine-formaldehyde condensate, a urea-formaldehyde condensate, a urea-glutaraldehyde condensate, a benzoguanamine-formaldehyde condensate, or a urea-glyoxal condensate.

The molar ratios of urea to formaldehyde are 1:2.5 to 1:3.5, preferably 1:2.7 to 1: 3.2.

If glutaraldehyde is used instead of formaldehyde, the molar ratios may be 1:1.5 to 1:2.5, preferably 1:1.8 to 1: 2.2.

The molar ratios of melamine to formaldehyde can be 1:3.5 to 1:8, preferably 1:4 to 1:6. The degree of etherification of these resins can be adjusted by the molar ratio of melamine to methanol and is typically c. 1:10 to 1:20, preferably c. 1:15 to 1:18.

Suitable amino resins for forming microparticles will be found, inter alia, in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd edition, Vol. 2, pp. 440-469.

The polycondensate is most preferably a melamine-formaldehyde condensate, a wholly or partially etherified melamine-formaldehyde condensate, or a urea-formaldehyde condensate.

The biologically active compound is preferably a pesticide or a mixture of pesticides, and is most preferably a herbicide, an insecticide, an acaricide, a nematocide, an ectoparasiticide, a fungicide or a mixture thereof.

Typical examples of pesticides are: urea derivatives, triazines, triazoles, carbamates, phosphoric acid esters, dinitroanilines, morpholines, acylalanines, pyrethroids, benzoic acid esters and polycyclic halogenated hydrocarbons.

Specific examples of pesticides suitable for use in the practice of this invention are listed hereinbelow (common names as given in The Pesticide Manual, 9th Edition, British Crop Protection Council):

Urea derivatives

Chlorbromuron, chloroxuron, chlorotoluron, fluometuron, thiazafluron and triasulfuron.

Halogenated acetanilides

Dimethachlor, alachlor, propachlor.

s-Triazines

Atrazine, propazine, terbuthylazine, ametryn, aziprotryne, cyromazine.

Triazole derivatives

Etaconazole, 1-[2-(2,4-dichlorophenyl)-pent-1-yl]-1H-1,2,4-triazole, triadimefon, difenoconazole.

Carbamates

Dioxacarb, aldicarb, benomyl.

Phosphoric acid esters

Methidathion, anilofos, azinphos methyl, fenamiphos, azamethiphos.

Dinitroanilines

Benfluralin, pendimethalin, butralin, fluchloralin.

Acylalanines

Metalaxyl, fluralaxyl, benzoylprop ethyl, flamprop methyl.

Pyrethroids

Cypermethrin, resmethrin, tetramethrin.

Benzilic acid esters

Bromopropylates, chlorobenzilates, chloropropylates.

Miscellaneous

Bromoxynil, ioxynil, oxadiazon, dicofol, fenoxycarb.

Preferred pesticides are S-2,3-dihydro-5-methoxy-2-oxo-1,3,4 thiadiazol-3-ylmethyl O,O-dimethyl phosphorodithioate (= methidathion), 2-phenylamino-4-methyl-6-cyclopropylpyrimidine and 3-(3-chloro-p-tolyl)-1,1-dimethylurea = chlorotoluron.

The hydrophobic wax may be a natural wax, a modified natural wax, or a semi-synthetic or fully synthetic wax.

The hydrophobic wax is preferably a vegetable wax, an animal wax, a montan wax, a paraffin wax, a polyolefin wax or an amide wax. Most preferably the hydrophobic wax is a macrocrystalline paraffin wax, a microcrystalline paraffin wax or a polyethylene wax.

The wax preferably has a melting point of 30 to 80°C.

In a preferred embodiment of the invention, the wax is used in an amount of 1 to 20 % by weight, most preferably of 5 to 15 % by weight, based on the biologically active compound or mixture thereof in the microcapsules.

In another of its aspects, the invention relates to a process for encapsulating biologically active compounds in the form of essentially spherical microcapsules, comprising the steps of

- a) preparing an aqueous solution of surfactants, catalysts and monomers, prepolymers or polymers which are suitable for forming a capsule wall,
- b) forming an emulsion or dispersion of the substantially water-insoluble biologically active compound or mixture thereof in the solution a) by adding said solution under high shear force, and
- c) forming a solid capsule wall around the biologically active compound or mixture thereof,

which process comprises blending the biologically active compound with a hydrophobic wax before forming the emulsion or dispersion b), melting the wax and adding the melt to the solution a).

A preferred embodiment of the process comprises fusing the biologically active compound and the wax together and adding the co-melt blend to the polymer solution.

It is particularly preferred to fuse the wax and the biologically active compound or mixture thereof together and to add this co-melt to the reaction solution a) at a temperature higher than that of said reaction solution a).

Another preferred embodiment of the process comprises dissolving the wax in a solvent, adding the solid active ingredient and cautiously evaporating the solvent, with stirring, to give a wax-coated active ingredient powder which can be used direct for the preparation of the microparticles.

The requirement must be made of the melt that the biologically active compound and the wax form a two-phase system at the temperature at which both are in the melt state and are not dissolved in each other.

The aqueous solution may contain, in addition to the monomers, prepolymers or polymers that form the capsule wall, one or more than one water-soluble monomer, oligomer or polymer as emulsifier or dispersant. Suitable emulsifiers or dispersants are anionic, cationic or nonionic substances. The surfactants customarily used in formulation technology are described, inter alia, in the following publications:

"Mc Cutcheon's Detergents and Emulsifiers Annual", Mc Publishing Corp., Glen Rock, NJ, USA, 1988",

H. Stache, "Tensid-Taschenbuch" (Handbook of Surfactants), 2nd edition, C. Hanser Verlag Munich, Vienna 1981,

M. and J. Ash. "Encyclopedia of Surfactants", Vol. I-III, Chemical Publishing Co., New York, 1980-1981.

The surfactants are polyethylene glycols, polyethylene glycol monoalkyl ethers, polyethylene glycol-polypropylene glycol copolymers, polyvinyl pyrrolidones and acrylic acid-acrylamide copolymers.

Methods of producing high shear forces are known per se. It is preferred to use a high-speed impeller or a rotary homogeniser.

In another of its aspects, the invention relates to a process for controlling plant pests,

weeds or animal parasites, which comprises suspending the novel microparticles in a biologically active concentration in water and applying the suspension so obtained to the pests or to the locus thereof.

In yet another of its aspects, the invention relates to the use of the novel microparticles for the preparation of a composition for controlling plant pests, weeds or animal parasites, and to water-dilutable powders, water-dispersible granules or aqueous spray mixtures containing said microparticles.

The invention is illustrated by the following Examples.

Examples for the preparation of the precondensates.

Example A1: Preparation of a modified melamine-formaldehyde precondensate

With stirring, 28 g of melamine (0.22 mol) are added to 124 ml of a 30 % aqueous solution of formaldehyde. The reaction mixture is adjusted with 1 N aqueous NaOH to pH 9 and heated to 94°C, whereupon the melamine dissolves while reacting with the aldehyde. The reaction mixture is then cooled to 62°C and, after addition of 120 ml of methanol (3.75 mol) and 7 ml of a 15 % aqueous solution of hydrochloric acid, the reaction is carried out at 62°C for 30 minutes. Then 2.8 g of triethanolamine are added and the azeotropic mixture of methanol-water is distilled from the reaction mixture. After adjustment to a solids content of c. 40 to 60 % by weight, 6 g of urea are added to the solution, which is then cooled to room temperature.

Example A2: Preparation of a urea-glutaraldehyde precondensate

With stirring, 60 g (1 mol) of urea are dissolved in 800 g (2 mol) of a 25 % aqueous solution of glutardiol aldehyde. The pH is adjusted with 1 N aqueous NaOH to 7-8 and the solution is then heated to a temperature of 70°C and stirred for 40 minutes at this temperature. The solution is afterwards cooled to room temperature.

Example for the preparation of the microparticles.

Example B1: 60 ml of water and 3 g of the precondensate prepared according to Example A1 as well as 0.15 g of polyethylene glycol (molecular weight 300) are charged to a reactor with temperature control. The reaction mixture is heated to 40°C and acidified

with 2.1 ml of 2N aqueous citric acid. Then 12.6 g of methidathion and 1.26 g of paraffin wax (m.p. 53°C) are fused together and homogenised. The melt is added rapidly to the reaction mixture, with stirring (Ultraturrax, 12 000 rpm), and stirred for 10 minutes at this speed. Stirring is afterwards continued with a paddle agitator at 500 rpm for 120 minutes at 60°C, giving a suspension of fine particles having average diameters of 1 to 10 µm. The suspension can be further used direct for a formulation or the particles can be dried to give a free-flowing powder. Electron micrographs show that the wax has deposited mainly on the inner wall of the microcapsule.

Example B2: 25 g of chlortoluron are mixed in a rotary evaporator with a 5 % solution of paraffin wax (m.p. 85°C) in petroleum spirit and the petroleum spirit phase is removed by evaporation until a finely particulate free-flowing powder is obtained. Then 140 ml of water and 30 g of the precondensate prepared in Example A1 as well as 21 ml of a 2N aqueous solution of citric acid are charged to a reactor with temperature control and the wax-treated chlortoluron is dispersed therein. The mixture is heated to 60°C and further stirred for 120 minutes. After cooling, a suspension of fine spherical particles having diameters of 1 to 10 µm is obtained. The suspension can be further used direct for a formulation or the particles can be dried to give a free-flowing powder. Electron micrographs show that the wax has deposited mainly on the inner wall of the microcapsule.

Example B3: The procedure of Example B2 is repeated, but using 70 g of the precondensate of Example A2, giving a suspension which can be further used direct for a formulation or the particles can be dried to give a free-flowing powder. Electron micrographs show that the wax has deposited mainly on the inner wall of the microcapsule.

What is claimed is:

1. Essentially spherical microparticles comprising a biologically active compound as core substance and a polymeric capsule material, wherein a hydrophobic wax forms a wax film as interlayer on the inside of the polymeric capsule wall and wholly or partially encapsulates the active ingredient.
2. Microparticles according to claim 1, wherein the average thickness of the wax layer is from 5 nm to 100 nm.
3. Microparticles according to claim 1, wherein the spherical microparticles have an average diameter of 0.5 to 500  $\mu\text{m}$ .
4. Microparticles according to claim 1, wherein the spherical microparticles have an average diameter of 0.5 to 100  $\mu\text{m}$ .
5. Microparticles according to claim 1, wherein the spherical microparticles have an average diameter of 0.5 to 20  $\mu\text{m}$ .
6. Microparticles according to claim 1, wherein the polymeric wall material is 5 to 40 % of the total weight of the microparticles.
7. Microparticles according to claim 1, wherein the polymeric wall material is a polyacrylate, a polyurethane, a polyester or an amino resin.
8. Microparticles according to claim 1, wherein the polymeric wall material is an amino condensation resin.
9. Microparticles according to claim 8, wherein the polycondensate is a melamine-formaldehyde condensate, a wholly or partially etherified melamine-formaldehyde condensate, a urea-formaldehyde condensate, a benzoguanamine-formaldehyde condensate, or a urea-glyoxal condensate.
10. Microparticles according to claim 9, wherein the a polycondensate is a melamine-formaldehyde condensate, a wholly or partially etherified

melamine-formaldehyde condensate or a urea-formaldehyde condensate.

11. Microparticles according to claim 1, wherein the biologically active compound is a pesticide or a mixture of pesticides.

12. Microparticles according to claim 11, wherein the biologically active compound is a herbicide, an insecticide, an acaricide, a nematocide, an ectoparasiticide, a fungicide or a mixture thereof.

13. Microparticles according to claim 12, wherein the biologically active compound is selected from S-2,3-dihydro-5-methoxy-2-oxo-1,3,4 thiadiazol-3-ylmethyl O,O-dimethyl phosphorodithioate (= methidathion), 2-phenylamino-4-methyl-6-cyclopropylpyrimidine and 3-(3-chloro-p-tolyl)-1,1-dimethylurea (=chlortoluron).

14. Microparticles according to claim 1, wherein the wax is a natural wax, a modified natural wax, a partially synthetic or a fully synthetic wax.

15. Microparticles according to claim 14, wherein the wax is a vegetable wax, an animal wax, a montan wax, a paraffin wax, a polyolefin wax or an amide wax.

16. Microparticles according to claim 15, wherein the wax is a macrocrystalline paraffin wax, a microcrystalline paraffin wax or a polyethylene wax.

17. Microparticles according to claim 14, wherein the wax has a melting point in the range from 30 to 80°C.

18. Microparticles according to claim 15, wherein the wax is present in the capsule in an amount of 1 to 20 % by weight, based on the biologically active compound or mixture thereof.

19. Microparticles according to claim 15, wherein the wax is present in the capsule in an amount of 5 to 15 % by weight, based on the biologically active compound or mixture thereof.

20. A process for encapsulating a biologically active compound in the form of essentially spherical microcapsules, comprising the steps of

- a) preparing an aqueous solution of surfactants, catalysts and monomers, prepolymers or polymers which are suitable for forming a capsule wall,
- b) forming an emulsion or dispersion of the substantially water-insoluble biologically active compound or mixture thereof in the solution a) by adding said solution under high shear force, and
- c) forming a solid capsule wall around the biologically active compound or mixture thereof,

which process comprises blending the biologically active compound with a hydrophobic wax before forming the emulsion or dispersion b), melting the wax and adding the melt to the solution a).

- 21. A process according to claim 20, which comprises fusing the biologically active compound and the wax together and adding the co-melt blend to the polymer solution.
- 22. A process according to claim 20, which comprises applying the wax from a solution to the biologically active compound and subsequently removing the solvent.
- 23. A process according to claim 21, which comprises fusing the wax and the biologically active compound or mixture thereof together and adding this co-melt to the reaction solution a) at a temperature higher than that of said reaction solution a).
- 24. A method of controlling plant pests, weeds or animal parasites, which comprises suspending microparticles as claimed in claim 1 in a biologically active concentration in water and applying the suspension so obtained to the pests or to the locus thereof.
- 25. The use of microparticles as claimed in claim 1 for the preparation of a composition for controlling plant pests, weeds or animal parasites.
- 26. A water-dilutable powder, a water-dispersible granular formulation or an aqueous spray mixture containing microparticles as claimed in claim 1.

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/EP 95/02729

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A01N25/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,90 02655 (ENCAPSULATION SYSTEMS INC) 22 March 1990 see page 8, line 33 see page 12, line 20-52 see page 18, line 18 - page 19, line 4 see page 22, line 29 - page 23, line 26 see figures ---	1-26
X	WO,A,90 00005 (REDDING BRUCE K JR) 11 January 1990 see page 12; example 3 see claims 1,10,11 --- -/--	1-26

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 102 806 (KONDO SADA0 ET AL) 25 July 1978  see column 1, line 57 - column 2, line 24 see column 7, line 24 see column 8, line 45-68 see claims 1,25-32 ---	1-7,11, 12, 14-20, 22,24-26
A	DATABASE WPI Section Ch, Week 8908 Derwent Publications Ltd., London, GB; Class A97, AN 89-059198 & JP,A,01 013 002 ( SUMITOMO CHEM IND KK) , 17 January 1989 see abstract -----	1,13

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9002655	22-03-90	EP-A- 0464023	08-01-92
WO-A-9000005	11-01-90	NONE	
US-A-4102806	25-07-78	JP-C- 1002105	19-06-80
		JP-A- 52031981	10-03-77
		JP-B- 53007149	15-03-78
		CA-A- 1071935	19-02-80
		GB-A- 1528419	11-10-78